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Certificate

The firm of Chemische Fabrik Stockhausen GmbH of 47805 Krefeld filed a patent application entitled

"Powdery cross-linked polymers capable of absorbing aqueous liquids and body fluids, a process for their production and their use"

with the German Patent Office on July 9, 1993.

The copy appended hereto is a true and exact reproduction of the originally filed document of this patent application.

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Powdery cross-linked polymers capable of absorbing aqueous liquids and body fluids, a process for their production and their use

The present invention relates to powdery, cross-linked polymers absorbing aqueous liquids and blood (superabsorbers) and having improved properties with regard to absorption velocity, swelling and retention capacity for aqueous liquids under high load. The present invention further relates to a process for the manufacture of said polymers and to their use in absorbent sanitary articles, such as diapers, in the adult incontinence, feminine hygiene, and for wound dressing.

Superabsorbers are water-insoluble, cross-linked polymers which, under swelling and formation of hydrogels, are capable of absorbing large amounts of aqueous liquids and body fluids, such as urine or blood, and of retaining the absorbed liquid amount under a certain pressure or load. Owing to said characteristic absorption properties the polymers are mainly used for incorporating them in sanitary articles, for example, diapers and sanitary napkins.

Initially, only the very high swelling capacity on contact with liquids, also referred to as free swelling capacity, had been the main factor in the development of superabsorbers; later it turned out, however, that not only the amount of absorbed liquid is of importance but also the stability of the swollen gel. However, absorbency, also referred to as swellability or free swelling capacity, on the one hand, and gel strength of a cross-linked polymer, on the other hand, represent contrary properties, as is known from U.S. Re No. 32,649. This means that polymers having a particularly high absorbency exhibit a poor strength of the swollen gel so that the gel is deformable under pressure (e.g., the load of a body) and further liquid distribution and absorption is prevented. According to U.S. Re 32,649 a balanced relation between absorption

capacity (gel volume) and gel strength is to be aimed at so as to ensure liquid absorption, liquid transport, dryness of the diaper and the skin when such superabsorbers are used in a diaper structure. In this connection, not only the polymer's capability of retaining a liquid under subsequent pressure, after swelling freely first, is of importance but also the fact that liquids are absorbed even against a simultaneously acting pressure, i.e. during the liquid absorption; this is the case in practice when a baby or person sits or lies on a sanitary article or when shear forces are acting, e.g., by movements of legs. In EP No. 0 339 461 this particular absorption property is referred to as absorption under load.

The only way to meet the increasing trend of reducing the size and thickness of sanitary articles for esthetic and environmental reasons (reduction of waste in the land fill) is to reduce the large-volume fluff pulp portion in diapers and to increase the portion of superabsorber at the same time. For that reason the superabsorber has to take over additional functions with respect to liquid absorption and transport thereof, which were previously performed by the fluff pulp and which cannot be accomplished by the known superabsorbers to a satisfactory extent.

This particularly applies to cases where the proportion of superabsorber in the absorbent zone of a sanitary article is increased to 40 to 60%-wt. and more. Owing to the poor absorption rate of the superabsorber in case of several mictions, so-called "leakage" may result caused by a blockade in the liquid transport and liquid distribution, in particular under pressure, i.e., the liquid is no longer absorbed by the sanitary article, thus resulting in a wet diaper surface and, consequently, wet skin.

To provide superabsorbent polymers having the characteristic properties, such as high absorption capacity, high gel strength and

high absorbency under load, it is necessary to subject the polymer resins to a subsequent surface treatment.

For example, U.S. Pat. No. 4 043 952 recommends polyvalent metal compounds to improve the dispersibility in water, and U.S. Pat. No. 4 051 086 proposes the use of glyoxal to improve the absorption rate. DE-OS 27 40 169 describes the production of absorbents based on potassium and ammonium acrylate-containing polymers which are treated with polyols and are used in diapers and other sanitary and medical articles in the form of powders and sheets. The secondary treatment of resins using cross-linking agents comprising bi- or polyfunctional groups capable of reacting with the carboxyl or carboxylate groups or other groups contained in the polymer is described in EP 0 083 022 (to improve the dispersibility in water and the absorbency), DE-OS 33 31 644 (to improve the resistance to salt solutions at high water absorption rates), DE-OS 35 07 775 (to increase the salt resistance with good liquid absorption and gel strength), DE-OS 35 23 617 (to improve flowability and prevent agglomeration), DE-OS 36 28 482 (to improve water absorption when used repeatedly), and EP 0 349 240 (to achieve a balance between absorbency and absorption rate as well as gel strength and suction force). In these cases, the powder is either directly mixed with the components, optionally with using small amounts of water and solvent, or dispersed in an inert solvent, or polymers comprising 10 to 40%-wt. of water are dispersed in a hydrophilic or hydrophobic solvent and mixed with the cross-linking agent, either subsequently or simultaneously. Suitable cross-linking agents include polyglycidyl ethers, halo epoxy compounds, polyols, polyamines, or polyisocyanates. Additionally, polyfunctional aziridine compounds, alkyl-di-(tri)-halogenides, and oil-soluble polyepoxy compounds are mentioned in DE-OS 33 14 019, EP 0 317 106, and DE-OS 37 37 196. In DE-OS 35 03 458 (to obtain a polymer having good water absorption capacity, high

water absorption rate and high gel strength in a non-tacky gel) the application of a cross-linking agent on a polymeric resin is effected in the presence of an inert inorganic powdery material, such as SiO_2 , without using organic solvents. According to DE-PS 40 20 780, an improved absorption under load is achieved by cross-linking the surface of a polymer resin with 0.1 to 5%-wt. of alkylene carbonate.

All these processes have in common that a temperature treatment of the resins is carried out subsequently.

The superabsorbers obtained according to the prior art have a high swellability under a load of 20 g/cm^2 , which, according to the teaching of DE-PS 40 20 780, amounts to 28 to 34 g/g for 0.9% solution of sodium chloride under this load (AUL). Additionally, it is reported that the products manufactured according to this patent have a high initial rate of liquid absorption under load so that 80% of the total capacity are achieved after only 15 minutes.

It turned out, however, that the relatively high absorption rate of the polymer resins obtainable by a secondary treatment according to the state of the art particularly exists if the liquid absorption takes place under a simultaneously acting load. However, in case of swelling without load the absorption must still be improved.

Additionally, the absorbent resins known from the art have the disadvantage that the swelling capacity substantially decreases under a load of more than 20 g/cm^2 . Accordingly, in a known polymer having an AUL of 30 g/g under a load of 20 g/cm^2 the AUL decreases to 15 g/g under a load of 40 g/cm^2 and to 9 g/g at 60 g/cm^2 . This reduction in the absorption capacity under high pressure has a particularly negative effect in new diaper structures with increased superabsorber proportions, in which the absorber

resin has to ensure the liquid transport to remote storing regions. In this case, owing to insufficient gel stability, a soft gel forms which deforms under a high pressure and that impairs further liquid transport due to the so-called "gel-blocking".

For the practical use of absorbent resins in sanitary articles a rapid liquid absorption under load-free swelling is very important since diapers for babies and pads for adults, for example, are not always subjected to a load by body weight, and in these cases a rapid absorption of large liquid amounts must also take place in order to prevent leakage.

Accordingly, it is the object of the present invention to provide superabsorbent polymers which, in addition to an improved absorption velocity and a high retention capacity, have a particularly high absorption under an increased load.

This object is achieved by a powdery, water-swellable, cross-linked polymer absorbing water, aqueous liquids, in particular body fluids, which polymer is formed of

- a) 55-99.9%-wt. of polymerized unsaturated, polymerizable, acid-groups-comprising monomers, said monomers being present as salts neutralized to the extent of at least 50 mole-%,
- b) 0-40%-wt. of polymerized unsaturated monomers which are copolymerizable with a),
- c) 0.1-5.0%-wt. of a cross-linking agent,
- d) 0-30%-wt. of a water-soluble polymer, with the sum of a)-d) amounting to 100%-wt,

and which polymer has an absorption capacity for a 0.9% NaCl-solution of at least 12 g/g polymer, preferably 16 g/g polymer at a load of 60 g/cm².

Most surprisingly it turned out that superabsorbent polymers having neutralized acid groups whose cations are selected from the group consisting of potassium, rubidium, cesium, ammonium, monomethyl ammonium, dimethyl ammonium, or trimethyl ammonium have a considerably improved absorption velocity if in the production of the polymer products, prior to the polymerization step, a blowing agent based on carbon dioxide has been added to the monomer solution. At the same time, the superabsorbers according to the invention have an improved absorption under a high load owing to the fact that the particulate absorbent resins have been treated with a reactive multifunctional secondary cross-linking agent and have then been heated to 120 - 300°C.

U.S. Pat. No. 4 529 739 describes absorbents which, starting from hydrophobic polymers in the form of latex, are manufactured by saponification under the addition of carbonates as blowing agents.

It is known from U.S. Pat. No. 5 118 719 to produce superabsorbent polymers having improved rate of water absorption by means of carbonate-containing blowing agents which, by releasing carbon dioxide, result in a hydrogel having a microcellular structure. As can be seen in the examples of U.S. Pat. No. 5 118 719, the absorption rate is improved, however, the absorption capacity reduced. Absorbent resins manufactured according to U.S. Pat. No. 5 118 719 have a considerably poorer absorption under load (AUL) than the products known from the art, e.g., those according to DE-PS 40 20 780. Even if the principle of adding a blowing

agent, according to the teaching of U.S. Pat. No. 5 118 719, is combined with the procedure according to DE-PS 40 20 780, no improvement in the absorption rate in case of swelling without load can be achieved, although there is a high absorption under a load of 20 g/cm². Thus, the aforementioned prior art does not contain any reference as to a way of how the property combinations of improved absorption rate in both unloaded and loaded absorption and improved absorption capacity under a high pressure can be achieved.

It was found that the cations of potassium, rubidium, cesium, as well as of ammonium, monomethyl ammonium, dimethyl ammonium or trimethyl ammonium, which are present in the salts resulting from the neutralization of the acid-group-containing monomers, have a decisive influence on absorption capacity and rate. It turned out that a considerable improvement in the absorption capacity under load and an improvement in the absorption rate occurred.

Preferred cations are the potassium ion and the ammonium ion.

Water-absorbing resins which may be used for the surface-cross-linking treatment are obtained by polymerizing 55-99.9%-wt. of monomers having acid groups, e.g., acrylic acid, methacrylic acid, 2-acrylamido-2-methylpropane sulfonic acid, or mixtures of these monomers; the acid groups are present in neutralized form to the extent of at least 50 mole percent. Particularly preferred is a resin formed of cross-linked acrylic acid or methacrylic acid which is neutralized to the extent of 50 to 80 mole percent.

Neutralization of the acid groups in the aqueous monomer solutions is effected with bases according to known methods, e.g., with lyes, carbonates or amines.

Preferred neutralizing agents are potash lye and ammonia. Further monomers suitable for the production of the water-absorbing resins include 0-40%-wt. of acrylamide, methacrylamide, hydroxyethyl acrylate, dimethylaminoalkyl(meth)-acrylate, dimethylaminopropyl acrylamide, or acrylamidopropyl trimethyl ammonium chloride. Proportions exceeding 40% of these monomers will deteriorate the swell capacity of the resins.

As cross-linking agent any compound may be used which has at least two ethylenically unsaturated double-bonds or one ethylenically unsaturated double-bond and one functional group reactive with acid groups, or several functional groups reactive with acid groups. Examples thereof include: acrylates and methacrylates of polyols, such as butanediol diacrylate, hexanediol dimethacrylate, polyglycol diacrylate, trimethylolpropane triacrylate, or allyl acrylate, diallyl acrylamide, triallyl amine, diallyl ether, methylene bisacrylamide, or N-methylol acrylamide.

0 to 30%-wt. partially or completely saponified polyvinyl alcohol, polyvinyl pyrrolidone, starch or starch derivatives, polyglycols, or polyacrylic acids may be comprised as water-soluble polymers in the water-absorbing resin. The molecular weight of said polymers is not critical provided that they are water-soluble. Preferred water-soluble polymers are starch or polyvinyl alcohol or mixtures of these polymers. The preferred content of said water-soluble polymers in the water-absorbing resin amounts to about 1-5%-wt., in particular if starch and/or polyvinyl alcohol are present as soluble polymers. The water-soluble polymers may be present as graft polymers having the acid-group-containing polymers.

In addition to resins obtained by cross-linking polymerization of partially neutralized acrylic acid, those are preferably used which

additionally comprise portions of graftpolymerized starch or of polyvinyl alcohol.

The production of the absorbent resins of the present invention is carried out according to known methods. It may either be effected by the aqueous solvent polymerization (gel process) or by the inverse emulsion/suspension polymerization.

According to the present invention, a blowing agent based on carbon dioxide as a carbonate or in the form of carbon dioxide, either gaseous or solid, must be dissolved or dispersed in the monomer solution or dispersion. A quantity of 0.1-5.0%-wt., relative to anhydrous polymer substance, e.g., of sodium carbonate, sodium hydrogencarbonate, potassium carbonate, potassium hydrogen-carbonate, ammonium carbonate, magnesium carbonate, calcium carbonate, or mixtures of these substances may be used as carbonates. If solid carbon dioxide (dry ice) is used, cooling of the monomer solution or dispersion to temperatures between -10°C. and 30°C., preferably between 0 and 10°C, and removal of oxygen may simultaneously be effected.

With respect to the surface-cross-linking treatment there are no specific limitations as to the particle shape of the absorber-resin used. The polymer may be present in the form of small beads obtained by inverse suspension polymerization, or in the form of irregularly shaped particles originating from drying and pulverizing the mass obtained by solvent polymerization. Drying of the hydrogel is effected at temperatures of 80-200°C., in particular at 100-180°., and preferably at 120-150°C. Usually, the particle size is between 20 and 3,000 μm , preferably between 50 and 1,000 μm .

For the surface-cross-linking treatment, the water-absorbing resins may be mixed with an aqueous-alcoholic solution of the secondary cross-linking agent. The amount of alcohol is determined by the solubility of the agent and is kept as low as possible for technical reasons, e.g., protection against explosions. Suitable alcohols are methanol, ethanol, butanol, or butyl glycol as well as mixtures of said alcohols. The preferred solvent is water which is used in an amount of 0.3-5.0%-wt., relative to resin. It is also possible to apply the secondary cross-linking agent from a powder mixture, e.g., using an inorganic carrier material, such as SiO_2 .

Alkylene carbonates according to DE-PS 40 20 780 are particularly preferred for the use as surface cross-linking agents.

To achieve the desired properties, the agent has to be distributed evenly on the resin powder. For this purpose, mixing is effected in suitable mixers, e.g., fluidized bed mixers, paddle mixers, milling rolls, or twin-worm-mixers.

It is also possible to carry out the treatment of the absorbent resin during one of the process steps in the production of the polymeric resin. To this end, a particularly suitable process is the inverse suspension polymerization.

The thermal treatment which follows the addition of the surface cross-linking agent is carried out at 100-300°C., preferably at 120-250°C. The temperature depends on the residence time and the kind of reactant. At a temperature of 150°C the thermal treatment must be carried out for several hours, whereas at 250°C a few minutes, e.g., 0.5 to 5 minutes, are sufficient to obtain the desired properties. The thermal treatment may be carried out in conventional dryers or ovens; examples thereof include rotary kilns, fluidized bed dryers, paddle dryers, disk dryers, or infrared dryers.

The treatment of cross-linking the surface of the absorbent resins may be effected once or several times.

The polymers according to the present invention may be manufactured on the large scale by continuous or discontinuous processes. The agents according to the present invention may be used for a variety of applications. If they are used, for example, as absorbing material in sanitary napkins and diapers, or for wound dressing purposes, they have the property to absorb rapidly large quantities of menstrual blood, urine or other body fluids. The absorbency and absorption velocity is absolutely superior to that of the known products. Since the agents of the invention absorb and retain the absorbed fluids under a high pressure load, they are particularly easy to use. They are particularly suitable for the use in concentrations that - relative to hydrophilic fiber material, e.g., fluff pulp - are higher than those possible to date.

In application, the proportion of the absorbing polymer may exceed 35%-wt.; it may amount to 15-100%-wt. and preferably 30-70%-wt., relative to the quantity formed by the absorbent polymer and the fluff. The polymers of the present invention stand out for an improved distribution of the fluid, in particular in the layers substantially containing polymer, immediately after liquid absorption.

Additionally, the polymers according to the present invention used as absorbents for water and aqueous liquids are useful in current-conducting and light-transmitting cables, in packaging materials and as soil improvers and artificial soil for plant breeding.

Test methods:

To characterize the water-absorbing resins, retention (TB), absorption under load (AUL) and absorption velocity/rate (AV and Vortex) were measured.

The retention is determined according to the tea bag method and reported as average value of three measurements. Approximately 200 mg of resin are enclosed in a tea bag and immersed in 0.9% NaCl-solution for 20 minutes. Then the tea bag is centrifuged in a centrifuge (diameter: 23 cm; rpm: 1,400) for 5 minutes and weighed. One tea bag without water-absorbing resin is used as blank.

$$\text{Retention} = \frac{\text{Weight} - \text{Blank reading}}{\text{Initial weight}} \quad [\text{g/g}]$$

The absorption under load (AUL) is determined according to the method described in EP 0 339 461, page 7: The initial weight of superabsorber is placed in a cylinder provided with sieve bottom, the powder is loaded by a piston exerting a pressure of 20 g/cm², 40 g/cm² and 60 g/cm². The cylinder is subsequently placed on a Demand-Absorbency-Tester (DAT), and the superabsorber is allowed to suck 0.9% NaCl-solution for one hour.

The absorption velocity (AV) is determined according to a modified form of the method Absorption under load (AUL), as described in EP 0 339 461, page 7. In this case, the absorption of the 0.9% solution of sodium chloride is measured without loading the powder with additional weights. After 15 s, 30 s, 1, 3, 5, 10 and 15 min. the absorbed quantity of liquid is determined by weighing. The measurement is carried out as triple determination.

The Vortex Test to determine the absorption rate is carried out following the method described in WO 87/03208 on page 9. The initial weight amounts to 2.0 g polymer; the time starting from sprinkling the polymer into the liquid until disappearance of the vortex is measured in seconds.

Examples

Comparative Example 1

According to example 4 of DE-PS 40 20 780, an aqueous monomer solution consisting of a mixture of sodium acrylate and acrylic acid, at a mole ratio of 70:30, and triallylamine as cross-linking agent is polymerized. The resultant gel is comminuted, dried, ground and screened out to a particle size ranging from 90 - 850 μm .

The powdery product is mixed with a mixture of 0.2/0.1/2.0% 1,3-dioxolan-2-one/water/ethanol, relative to powder, and heated to 180°C. for 1 hour.

The product properties are shown in Table 1.

Comparative Example 2

According to example 4 of U.S. Pat. No. 5,118,719, an aqueous monomer solution consisting of a mixture of sodium acrylate and acrylic acid, at a mole ratio of 70:30, and triallyl amine as cross-linking agent is polymerized after addition of 0.5% basic magnesium carbonate. The resultant gel is comminuted, dried, ground, and screened out (90-850 μm).

Comparative Example 3

Comparative Example 1 is repeated. However, prior to polymerization, 0.5% basic magnesium carbonate as CO_2 -releasing blowing agent is added to the monomer solution, as described in U.S. Pat. No. 5,118,719. The resultant powdery polymer is subjected to the same secondary treatment as in Comparative Example 1.

The product properties are shown in Table 1.

Table 1

Comparative Example	1	2	3	
TB	30	26	30	g/g
AUL 20 g/cm ²	30	20	30	g/g
40 g/cm ²	15	9	16	g/g
60 g/cm ²	9	8	8	g/g
Vortex	83	18	66	s
AV 15 s	2	7	3	g/g
30 s	4	15	6	g/g
1 min	9	24	11	g/g
3 min	19	33	26	g/g
5 min	25	36	31	g/g
10 min	34	37	36	g/g
15 min	39	37	39	g/g

TB = Tea bag test

AUL = Absorption under load

AV = Absorption velocity

Examples 1 - 7

An aqueous monomer solution consisting of a mixture of

Example 1: potassium acrylate

Example 2: potassium acrylate

Example 3: potassium acrylate

Example 4: potassium acrylate

Example 5: ammonium acrylate

Example 6: methyl ammonium acrylate

Example 7: cesium acrylate

and acrylic acid at a mole ratio of 70/30 and triallyl amine as cross-linking agent was polymerized under addition of a carbonate and 0-1% polyvinyl alcohol (PVA). The resultant gel was comminuted, dried, ground and screened out to 90-850 μm .

The powdery, screened polymer was mixed with a mixture of 1,3-dioxolan-2-one or ethylene glycol diglycidyl ether (EGDE), water and ethanol and heated to 120-300°C. for 0.5-1 hour.

Examples 8 and 9

An aqueous monomer solution consisting of a mixture of

Example 8: potassium acrylate

Example 9: ammonium acrylate

and acrylic acid, at a mole ratio of 70/30, and triallylamine as cross-linking agent with the addition of 0-1% polyvinyl alcohol (PVA) was saturated with carbon dioxide (by introducing dry ice) and then polymerized. The resultant gel was comminuted, dried, ground and screened out to 90-850 μm .

The powdery, screened polymer was mixed with a mixture of 1,3-dioxolan-2-one and ethylene glycol diglycidyl ether (EGDE), water and ethanol and heated to 120-300°C. for 0.5-1 hour.

Composition, reaction conditions, and product properties are listed in Table 2.

Table 2

Example	1	2	3	4
Cation	K	K	K	K
Cross-linker [%]	0.4	0.4	0.4	0.5
Carbonate [%]	1.5 potass.	2.5 potass.	1.5 potass.	0.5 potass.
PVA [%]	1.0	1.0	-	1.0
1,3-dioxolan-2-one [%]	0.5	0.5	0.5	0.5
Water [%]	2.0	2.0	2.0	2.0
Ethanol [%]	4.0	2.0	2.0	2.0
Time [min]	30	30	30	30
Temperature [C]	200	180	200	200
TB	27	28	27	27 g/g
AUL 20 g/cm ²	25	28	27	25 g/g
40 g/cm ²	20	20	22	23 g/g
60 g/cm ²	18	14	18	21 g/g
Vortex	21	16	21	23 s
AV 15 s	12	10	10	9 g/g
30 s	19	20	16	16 g/g
1 min	26	28	24	23 g/g
3 min	36	38	31	33 g/g
5 min	38	43	33	35 g/g
10 min	39	44	35	36 g/g
15	40	45	37	38 g/g

Table 2 continued

Example	5	6	7	8	9
Cation	NH ₄	NH ₃ CH ₃	Cs	K	NH ₄
Cross-linker [%]	0.3	0.3	0.3	0.3	0.3
Carbonate	1.5NH ₄ ⁺	1.5NH ₄ ⁺	1.5 Cs	CO ₂	CO ₂
Saturation					
temp. °C	-	-	-	4	13
Polyvinyl					
alcohol	-	-	-	1.0	1.0
EGDE	0.25	-	-	-	0.25
1,3-dioxolan-					
2-one	-	1.0	0.5	0.5	-
Water	2.0	8.0	2.0	2.0	2.0
Ethanol	2.0	8.0	2.0	2.0	2.0
Time [min]	60	60	30	30	60
Temperature[°C]	120	140	200	200	120
TB	33	35	20	27	33 g/g
AUL 20 g/cm ²	28	24	19	25	29 g/g
40 g/cm ²	22	17	15	20	23 g/g
60 g/cm ²	18	12	11	16	17 g/g
Vortex	27	28	32	15	12 s
AV 15 s	8	6	3	12	14 g/g
30 s	13	12	10	17	20 g/g
1 min	19	18	17	28	27 g/g
3 min	31	26	22	36	36 g/g
5 min	34	29	24	40	41 g/g
10 min	40	34	27	43	44 g/g
15	42	37	28	44	45 g/g

Claims

1. A powdery, water-swellable, cross-linked polymer absorbing water, aqueous liquids, in particular body fluids, which polymer is formed of
 - a) 55-99.9%-wt. of polymerized unsaturated, polymerizable, acid-groups-comprising monomers, said monomers being present as salts neutralized to the extent of at least 50 mole-%,
 - b) 0-40%-wt. of polymerized unsaturated monomers which are copolymerizable with a),
 - c) 0.1-5.0%-wt. of at least one cross-linking agent,
 - d) 0-30%-wt. of a water-soluble polymer, with the sum of a)-d) amounting to 100%-wt.,characterized in that the polymer has an absorption capacity for 0.9% NaCl-solution of at least 12 g/g polymer, preferably 16 g/g polymer at a load of 60 g/cm².
2. The polymer according to claim 1 characterized in that the polymer has an absorption capacity for 0.9% NaCl-solution of at least 10 g/g polymer, preferably 16 g/g polymer, within 30 seconds.
3. The polymers according to claim 1 or 2 characterized by a particle size of 20 to 3,000 μm , preferably of 100 to 1,000 μm .
4. A powdery, water-swellable, cross-linked polymer absorbing water, aqueous liquids, in particular body fluids, which polymer is formed of

- a) 55-99.9%-wt. of polymerized unsaturated, polymerizable, acid-groups-containing monomers, said monomers being present as salts neutralized to the extent of at least 50 mole-%,
- b) 0-40%-wt. of polymerized unsaturated monomers which are copolymerizable with a),
- c) 0.1-5.0%-wt. of at least one cross-linking agent,
- d) 0-30%-wt. of a water-soluble polymer, with the sum of a)-d) amounting to 100%-wt,

characterized in that the salts according to a) comprise as cations K^+ , Cs^+ , Rb^+ and ammonium ions, as well as primary, secondary, and tertiary methyl ammonium ions, either alone or in combination, that 0.1-5.0%-wt., relative to the polymer, of a blowing agent based on carbon dioxide has been added to the monomers prior to polymerization, that the polymer has been dried, one or several compounds, or their solution or dispersion, which are reactive for secondary surface-cross-linking have been added thereto and that it has been heated to a temperature of 100-300°C.

5. The polymers according to claims 1 to 4 characterized in that the acid-group-containing monomers a)

are selected from the group consisting of acrylic acid, methacrylic acid, acrylamidomethylpropane sulfonic acid, and mixtures of these monomers,

the monomers b)

are selected from the group consisting of acrylamide, methacrylamide, hydroxyalkyl acrylate, dimethylaminoalkyl-(meth)-acrylate, dimethylaminopropyl(meth)acrylamide, the quaternary amine and ammonium salts of these monomers, and of mixtures of these monomers,

the cross-linking agent c)

is selected from the group consisting of alkylene bisacrylamide, N-methylol acrylamide, butanediol diacrylate, hexanediol dimethacrylate, polyglycol diacrylate, trimethylol-propane triacrylate, allyl acrylate, diallyl acrylamide, triallyl amine, diallyl ether, or mixtures of these cross-linking agents,

and that the blowing agent based on carbon dioxide is a carbonate selected from the group consisting of Na_2CO_3 , K_2CO_3 , $(\text{NH}_4)_2\text{CO}_3$, MgCO_3 , CaCO_3 , NaHCO_3 , KHCO_3 , mixtures of these carbonates, or carbon dioxide in gaseous or solid form.

6. A process for the production of the polymers according to claims 1 to 5 by polymerizing the monomers a), the monomers b) which are copolymerizable with a), and the cross-linking agent c) in the presence of the water-soluble polymer d), which process is characterized in that the salts according to a) are selected from the group consisting of ions of potassium, cesium, rubidium, ammonium, of primary, secondary and tertiary methyl ammonium, or of mixtures of these ions, that 0.1-5.0%-wt., relative to the polymer, of a blowing agent based on carbon dioxide is added to the monomers prior to polymerization, that polymerization of the obtained monomer mixture is effected under addition of radical forming initiators or by initiation by exposure to light or irradiation under formation of a hydrogel, that the polymer is dried, that one

or several compounds, or their solution or dispersion, which are reactive for secondary near-surface cross-linkage are added to the polymer and that this is heated to a temperature of 100-300°C.

7. The process according to claim 6 characterized in that the polymer is dried at temperatures of 80 to 200°C., in particular of 100 to 180°C., and preferably of 120 to 150°C.

8. The process according to claim 6 characterized in that the polymer is ground after drying.

9. The process according to claim 7 or 8 characterized in that the polymer is screened out to a particle size of 20 - 3,000 μm , preferably of 50 - 1,000 μm .

10. The process according to claim 6 characterized in that heating to a temperature of 100 to 300°C. is effected for near-surface cross-linkage.

11. The process according to claim 6 characterized in that the polymerization is effected in aqueous solution.

12. The process according to claim 6 characterized in that the polymerization is effected in a w/o-dispersion.

13. The use of the polymers according to claims 1 to 5 as component in sanitary articles which absorb body fluids and in wound dressings.

14. The use of the polymers according to claims 1 to 5 as component in diapers, sanitary napkins, and incontinence articles.

15. The use of the polymers according to claims 1 to 5 in diapers in a weight percentage, relative to the weight amount of polymer and fluff, of 15 - 100%-wt., preferably 35 - 100%-wt., and most preferably of 30 to 70%-wt.
16. The use of the polymers according to claims 1 to 5 as component in current-conducting and light-transmitting cables.
17. The use of the polymers according to claims 1 to 5 as soil conditioner.
18. The use of the polymers according to claims 1 to 5 as artificial soil for plant breeding.
19. The use of the polymers according to claims 1 to 5 as component in packaging materials.